

# Folded modes in the infrared spectra of the spin-Peierls phase of CuGeO<sub>3</sub>

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Polarized far-infrared transmittance spectra of CuGeO<sub>3</sub> single crystals were measured at different temperatures (6 K < T < 300 K). Two spectral lines, at 284.2 cm<sup>-1</sup> in E||c polarization and at 311.7 cm<sup>-1</sup> in E||b polarization, appear at the temperature of the spin-Peierls transition and grow in intensity with decreasing temperature. We assign these spectral features to the folded modes of the dimerized lattice. We discuss a possible role of the spin-phonon interaction in the formation of the 311.7 cm<sup>-1</sup> feature.

CuGeO<sub>3</sub> has attracted a considerable attention as the first inorganic compound that undergoes the spin-Peierls transition [1]. The spin-Peierls transition is known to occur in quasi-one-dimensional s=1/2 Heisenberg antiferromagnets due to the magnetoelastic coupling between magnetic chains and a three-dimensional phonon field. As a result of this coupling, magnetic atoms displace along the chain and form nonmagnetic dimers yielding a singlet ground state and a triplet excited state at an energy  $\Delta$  (the spin-Peierls gap).

In the high-temperature phase of CuGeO<sub>3</sub> (space group Pbmm, z=2, lattice parameters a=0.480 nm, b=0.847 nm, and c=0.294 nm [2]), S=1/2 Cu<sup>2+</sup> ions occupy C<sub>2h</sub> symmetry positions in the centra of strongly deformed edge-sharing Cu(O<sub>2</sub>)<sub>4</sub>(O<sub>1</sub>)<sub>2</sub> octahedra that form chains along the c-axis of the crystal (see Fig. 1). The octahedra from the neighboring chains share common O<sub>1</sub> apical oxygens. As the Cu–O<sub>1</sub> distances (0.275 nm) are appreciably greater than the Cu–O<sub>2</sub> distances (0.193 nm), well isolated ribbons of Cu(O<sub>2</sub>)<sub>4</sub> rectangles running along the c-axis may be considered as main magnetic units.

Below  $T_{sp} \approx 14$  K the Cu<sup>2+</sup> chains distort into dimers and the spin-Peierls gap  $\Delta_1 = 2$  meV = 16 cm<sup>-1</sup> opens at the point  $\mathbf{k}_{AF} = (0, 1, 1/2)$  of the Brillouin zone (BZ) [3,4]. The narrowest gap is shifted from the  $\mathbf{k} = 0$  point because of the interchain interaction. A second gap  $\Delta_2 = 5.5$  meV = 44.3 cm<sup>-1</sup> has been found in the electron spin resonance [5] and far infrared (FIR) absorption [6] experiments and has been assigned to the point  $\mathbf{k} = (0, 0, 0)$ . In a recent theoretical paper [7] it was, however, suggested to place this gap at the point  $\mathbf{k} = (0, 1, 0)$ . X-ray, neutron and electron diffraction studies revealed superlattice reflections that have been indexed with a commensurate propagation vector  $\mathbf{k}_{sp} = (1/2, 0, 1/2)$  corresponding to a crystal unit cell doubled along the c- and a-directions (see, e. g., [2] and references therein). This

doubling of the unit cell leads to a folding of the Brillouin zone and, as a result, to a transfer of phonons from the zone boundary to its center. The structure of the spin-Peierls phase belongs to the Bbcm space group [2]. The factor group analysis shows that additional eighteen Raman active modes  $4A_g + 5B_{1g} + 4B_{2g} + 5B_{3g}$  and nine IR active modes  $2B_{1u}(E||c) + 4B_{2u}(E||b) + 3B_{3u}(E||a)$  have to appear in the spin-Peierls phase of CuGeO<sub>3</sub>. (Here, symmetries of the vibrational modes are given according to the axes setting x||a, y||b, z||c).

The Raman peaks at 369 and 820 cm<sup>-1</sup> have been attributed to the  $A_g$  folded modes [8–10]. The feature at 43.5 cm<sup>-1</sup> observed in the far-infrared absorbance difference spectra  $\alpha(T) - \alpha(15.5$  K) below  $T_{sp}$  has been supposed to arise from the folded mode corresponding to a TA phonon at the  $a^*$  zone boundary [6]. The authors of Ref. [6] could not investigate how does the 43.5 cm<sup>-1</sup> feature behave when approaching  $T_{sp}$ , because of its proximity to the relatively strong 44.3 cm<sup>-1</sup> peak due to the  $\Delta_2$  spin gap. The 311.7 cm<sup>-1</sup> feature observed in both transmittance  $T_r(20\text{ K})/T_r(6\text{ K})$  [11] and reflectance  $R(20\text{ K})/R(5\text{ K})$  [12] ratios for CuGeO<sub>3</sub> has been ascribed to a softening of the  $B_{2u}$  ( $B_{3u}$  in Pmma setting) phonon mode near 300 cm<sup>-1</sup> when passing through the 14 K spin-Peierls transition to the dimerized state [12]. All the above mentioned IR measurements have been performed using unpolarized light and relatively thick samples with saturated absorption by phonons.

Recently, we have shown that lattice dimerization in the course of the spin-Peierls transition in NaV<sub>2</sub>O<sub>5</sub>, in contrast to the case of CuGeO<sub>3</sub>, leads to the appearance of numerous folded modes in the FIR transmittance spectra with typical integrated intensities  $\int d\omega \alpha \approx 100 - 400$  cm<sup>-2</sup> [13]. In attempt to clarify the nature of such a puzzling difference between these two recently discovered inorganic spin-Peierls compounds, we have undertaken the present study. This paper reports on a direct measurement of the polarized FIR transmittance spectra of CuGeO<sub>3</sub> as a function of temperature. In the spectral range studied (60–400 cm<sup>-1</sup>), we clearly observe the appearance of two absorption lines (at 284.2 and 311.7 cm<sup>-1</sup>) at the temperature of the spin-Peierls transition. We attribute these spectral features to the folded modes which occur due to lattice dimerization in the spin-Peierls phase and speculate that the spin-phonon interaction contributes to the 311.7 cm<sup>-1</sup> absorption line.

Blue in color transparent single crystals of CuGeO<sub>3</sub> were grown from the melt of high purity oxides by a method of spontaneous crystallization under a slow cooling. They were checked with X-ray diffraction and magnetization measurements and exhibited the temperature of the spin-Peierls transition  $T_{sp} = 14.0 \pm 0.2$  K. Three samples cleaved perpendicular to the  $a$ -axis and having dimensions approximately 3×3 mm along the  $b$ - and  $c$ -axes were used in our experiments. Their thicknesses were 240, 20±1 and 0.7±0.1 μm. The thinnest sample was on a Scotch tape. Samples were mounted in a special insert that was put into a variable temperature ( $T=5\text{--}300$  K) helium vapor optical cryostat. Polarized infrared transmission measurements were performed in the frequency range from 60 to 400 cm<sup>-1</sup> with the spectral resolution 0.2–1 cm<sup>-1</sup>, using a BOMEM DA3.002 Fourier transform spectrometer. To avoid possible errors connected with a thermal displacement of a sample relative to the radiation beam within the spectrometer we measured reference spectra at each temperature. Our insert has been specially constructed for such a procedure. In our experimental geometry ( $\mathbf{k} \parallel \mathbf{a}$ ) we could anticipate to find four new  $B_{2u}$  modes in  $\mathbf{E} \parallel \mathbf{b}$  polarization and two new  $B_{1u}$  modes in  $\mathbf{E} \parallel \mathbf{c}$  polarization below  $T_{sp}$ .

Fig. 2a shows the transmittance spectrum in  $\mathbf{E} \parallel \mathbf{b}$  polarization of the 20 μm thick sample at temperatures above and below  $T_{sp}$ . Two well known [14]  $B_{2u}$  phonon modes near 220 and 300 cm<sup>-1</sup> are seen in the displayed spectral range. From the intervals of zero transmittance we determine the corresponding transverse and longitudinal frequencies. We find  $\omega_{TO}=210$  and 284 cm<sup>-1</sup>,  $\omega_{LO}=233$  and 310 cm<sup>-1</sup> at room temperature, in good agreement with parameters found from the best oscillator-fit of reflectivity spectra [14]. The structure with regularly changing period in Fig. 2a comes from the interference in the platelet, taking into account the changes of the refractive index in the vicinity of a phonon frequency. We have confirmed such an interpretation by direct calculations of transmittance spectra of a platelet with a given thickness and the dielectric constant taken from the Ref. [14]. The main change in the spectrum when passing through the spin-Peierls transition temperature is a blue shift of the high frequency edge of the phonon mode near 300 cm<sup>-1</sup>.

To investigate this phenomenon, we have measured the 0.7 μm thick sample. Two sharp peaks at the  $\omega_{TO}$  frequencies are present in its spectrum (see the spectrum *b* in Fig. 2). It is clearly seen that a new spectral line at 311.7 cm<sup>-1</sup> appears below  $T_{sp}$ . Fig. 3a demonstrates how does this line grow in intensity with decreasing temperature. We did not observe any softening of the 288 cm<sup>-1</sup> phonon mode near  $T_{sp}$ . This mode smoothly shifts to higher frequencies when going from the room temperature down to 6 K.

In the  $\mathbf{E} \parallel \mathbf{c}$  spectrum of the uniform phase, only one phonon mode is present (at 165 cm<sup>-1</sup>), and it is narrow ( $\omega_{LO} - \omega_{TO} = 3$  cm<sup>-1</sup>). So, we were able to measure transmittance of thick samples. The spectra of the 240 μm

thick sample revealed a new spectral line at 284.2 cm<sup>-1</sup> that appeared below  $T_{sp}$  (see Fig. 3b).

Table 1 lists the parameters of the two observed lines. For both of them, the position and the full width at half height (FWHH) do not depend on the temperature, within the experimental precision. The normalized integrated intensity versus temperature dependences are practically identical for both lines (see the results for the 240 μm and 20 μm thick samples presented in Fig. 4). The shift of the transition temperature to  $T_{sp}=15.2$  K for the thinnest sample may be due to internal stress within this 0.7 μm thick platelet on a Scotch tape (it is known that  $T_{sp}$  becomes higher under pressure [15]). The same might be the reason for a broader line in this sample as compared to the 20 μm thick sample. At  $T > T_{sp}$  both lines are absent, within the precision of our measurements which may be estimated as 10 % for the 284.2 cm<sup>-1</sup> line and 5 % for the 311.7 cm<sup>-1</sup> one, taking into account the signal-to-noise ratio in our spectra and the measurements of the samples of different thickness.

Let us discuss the possible nature of the observed FIR absorption lines. We shall consider purely magnetic, purely phonon and mixed absorption which could occur in the spin-Peierls phase of CuGeO<sub>3</sub>. In this phase, well defined magnonlike triplet excitations have been observed by inelastic neutron scattering (INS) [3]. Their frequencies show a noticeable dispersion in the  $b^*$  and  $c^*$  directions of the BZ. A singlet-triplet transition has been observed as a FIR absorption peak at 44.3 cm<sup>-1</sup> that splits in a magnetic field [6]. Absorption with creation of two magnons ( $\mathbf{k}$  and  $-\mathbf{k}$ ) would reflect a magnon density of states. Then, one could expect spectral features at the doubled frequencies corresponding to flat area in the dependence  $\omega(\mathbf{k})$ , namely, at  $2\Delta_1 = 32$  cm<sup>-1</sup>,  $2\Delta_2 = 90$  cm<sup>-1</sup>,  $2\omega_m = 255 \pm 7$  cm<sup>-1</sup> [3,4],  $\omega_m$  corresponding to the maximum of the dispersion curve. A possible magnon-magnon interaction would somewhat lower these frequencies. The frequencies of the discussed FIR spectral lines, 284.2 and 311.7 cm<sup>-1</sup>, lie higher than the mentioned frequencies which rules out their interpretation as features due to two-magnon (2M) absorption. It should be mentioned that for CuGeO<sub>3</sub> the most important term in the 2M absorption Hamiltonian vanishes by symmetry considerations [16], in contrast to the case of another spin-Peierls compound, NaV<sub>2</sub>O<sub>5</sub>, where 2M absorption is allowed. For NaV<sub>2</sub>O<sub>5</sub>, indeed, we succeeded to observe it [13].

Another absorption process that involves magnetic excitations is a phonon-assisted two magnon (P+2M) absorption which may be particularly important when 2M absorption is forbidden (see, e. g., [16]). Critical points in the densities of phonon and magnon states contribute to P+2M absorption peaks. Because of that, magnetic excitations with energies  $\Delta_1$ ,  $\Delta_2$  and  $\omega_m$  have to be taken into consideration. All of them broaden dramatically with increasing temperature. Besides, the gap modes shift to zero when approaching  $T_{sp}$ . If the observed spectral features (at 284.2 and 311.7 cm<sup>-1</sup>) were due to

P+2M absorption they would shift and/or broaden with increasing temperature towards  $T_{sp}$ . This is not the case, within the precision of our experimental data.

The absence of any broadening or shift of the observed FIR absorption lines at 284.2 and  $311.7\text{ cm}^{-1}$  with approaching  $T_{sp}$  from below rules out a participation of magnetic excitations in their formation. To our mind, the FIR absorption lines at 284.2 and  $311.7\text{ cm}^{-1}$  result from zone boundary phonons activated by the zone folding due to the lattice dimerization in the spin-Peierls phase. Unfortunately, the frequencies of zone boundary phonons are known (from INS) only up to about  $180\text{ cm}^{-1}$  [17], so, no comparison with the frequencies of the observed FIR modes can be made. The intensity of folded modes should be proportional to squared displacements of atoms in the course of the spin-Peierls transition,  $I(T) \propto \delta^2(T)$ , just as in the case of superlattice reflections in X-ray or inelastic neutron scattering. Our experimental  $I(T)$  dependences displayed in Fig. 4 are similar to those reported from INS [4], which is in agreement with the interpretation of the peaks at 284.2 and  $311.7\text{ cm}^{-1}$  as folded modes.

The peak at  $311.7\text{ cm}^{-1}$  is much stronger and broader than the one at  $284.2\text{ cm}^{-1}$  (see Table 1). We suppose, the reason for that lies in a relatively strong spin-phonon coupling for the former mode. Recent neutron diffraction experiments have shown that the deformation of the lattice above  $T_{sp}$  may be characterized by a rotation of the  $\text{Cu}(\text{O}_2)_4$  ribbons around the  $c$ -axis and has the  $A_g$  symmetry [2]. It is related to the distortion below  $T_{sp}$ , in the sense that the rotation of the O2 edges around the  $c$ -axis is the common element. In the high-temperature deformation the edges stacked along the  $c$ -axis are displaced in the same way, whereas below  $T_{sp}$  neighboring edges are displaced in opposite directions resulting in the twist distortion. Both deformations strongly influence the magnetic interaction parameter  $J$  [2]. Keeping that in mind, we propose the zone boundary counterpart of the  $A_g$  mode at  $332\text{ cm}^{-1}$  [14] as a candidate for a phonon responsible for the observed  $311.7\text{ cm}^{-1}$  feature. At the zone center, this mode tends to rotate  $\text{Cu}(\text{O}_2)_4$  ribbons around the  $c$ -axis [14] while at the zone boundary it corresponds to the twist rotations of the neighboring O2–O2 edges. It seems evident from the results of the work [2] that this mode efficiently modulates the superexchange interaction and, thus, is strongly coupled to spins. In the spin-Peierls phase  $A_g$  mode splits into  $A_g + B_{3g} + B_{1u} + B_{2u}$  where the latter is indeed IR active in  $\mathbf{E} \parallel \mathbf{b}$  polarization.

In summary, our measurements of polarized FIR transmittance spectra of  $\text{CuGeO}_3$  have unambiguously shown that the  $B_{2u}$  mode near  $300\text{ cm}^{-1}$  does not soften upon passing through the 14 K spin-Peierls transition, as has been stated in Ref. [12], but a new mode with the frequency  $311.7\text{ cm}^{-1}$  appears. Another mode, of  $B_{1u}$  symmetry, appears at  $284.2\text{ cm}^{-1}$ . Both modes are, most likely, transferred to the zone center from the zone boundary, due to lattice dimerization. We propose a possible

mechanism of the spin-phonon coupling contributing to the  $311.7\text{ cm}^{-1}$  mode.

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FIG. 1. Crystal structure of CuGeO<sub>3</sub>. The axes are shown in the *Pbmm* setting.

FIG. 2. Transmittance spectra of (a) 20  $\mu\text{m}$  and (b) 0.7  $\mu\text{m}$  thick samples of CuGeO<sub>3</sub> for  $\mathbf{E} \parallel \mathbf{b}$  polarization; solid lines —  $T = 6\text{ K} < T_{\text{sp}}$ , dashed line —  $T = 30\text{ K} > T_{\text{sp}}$ .

FIG. 3. FIR absorption lines activated by the spin-Peierls transition in CuGeO<sub>3</sub>: (a)  $\mathbf{E} \parallel \mathbf{b}$ , 0.7  $\mu\text{m}$  thick sample; (b)  $\mathbf{E} \parallel \mathbf{c}$ , 240  $\mu\text{m}$  thick sample.

FIG. 4. Temperature dependences of the integrated intensity  $I(T) = \int d\omega [\alpha(T, \omega) - \alpha(20\text{ K}, \omega)]$  for the lines at 284.2  $\text{cm}^{-1}$  (circles — 240  $\mu\text{m}$  thick sample) and 311.7  $\text{cm}^{-1}$  (squares — 20  $\mu\text{m}$  thick sample, triangles — 0.7  $\mu\text{m}$  thick one).

TABLE I. Parameters at  $T = 6\text{ K}$  of the FIR absorption lines activated by the spin-Peierls transition in CuGeO<sub>3</sub>

Polarization	$\mathbf{E} \parallel \mathbf{c}$	$\mathbf{E} \parallel \mathbf{b}^\dagger$
Frequency $\omega$ , $\text{cm}^{-1}$	284.24 $\pm$ 0.05	311.70 $\pm$ 0.05
FWHH $\Delta\omega$ , $\text{cm}^{-1}$	0.55 $\pm$ 0.05	4.5 $\pm$ 0.5 <sup>‡</sup>
Peak absorption coefficient $\alpha_m$ , $\text{cm}^{-1}$	9.3 $\pm$ 0.3	500 $\pm$ 100
Integrated intensity, $\text{cm}^{-2}$	6 $\pm$ 0.5	2500 $\pm$ 500

<sup>†</sup>data for the 0.7  $\mu\text{m}$  thick sample.

<sup>‡</sup>3.5  $\pm$  0.5 for the 20  $\mu\text{m}$  thick sample.

Cu   ●   O   ●   Ge   ●









